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Special Bulletin: Heating  
Power of Wyoming Coal & Oil

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UNIVERSITY OF WYOMING.

LARAMIE, WYOMING.

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Departments of Chemistry and Mechanical Engineering.

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SPECIAL BULLETIN.

JANUARY, 1895.

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# The Heating Power of Wyoming Coal and Oil

With a Description of the Bomb Calorimeter.

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Professor of Mechanical Engineering.

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TO THE  
AIRBORNE



# THE HEATING POWER

—OF—

## WYOMING COAL AND OIL

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### INTRODUCTORY.

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The value of a fuel depends upon the amount of heat that can be obtained from it. Although we buy it by weight, it is not matter we want, but energy. Everyone who uses fuel either for heat or power needs to know what is the greatest amount of heat that can be obtained from the kind of fuel used. He can then tell whether he is getting that which is the best quality for the price paid and also whether he is getting as large a proportion as he should of the total heat.

As coal is at present the most important of the mineral resources of Wyoming, it was thought that the State University could hardly do a greater service to consumers as well as mine-owners than to make a complete and impartial investigation of the relative and absolute value of the coal from different localities. We give accordingly a comparative table of the heating value of Wyoming coals so far as we could obtain samples of them, and also a table of the fuel value of the crude petroleum of Wyoming. Following this is a description of the calorimeter used, as it is an instrument which will probably come into general use

and, so far as we know, no complete description of the apparatus and its manipulation has yet been published in English.\*

COLLECTION OF SAMPLES.

The most essential part of an investigation like the present is the selection of samples accurately representing the coal fields from which they are taken. This task was efficiently performed by W. C. Knight, Professor of Geology in the University of Wyoming, who personally visited most of the coal- and oil-fields of the State during the summers of 1893 and 1894.† The samples were obtained by cutting down the whole face of the exposed coal-bed, rejecting partings and slates, breaking up and dividing until a sample of five to ten pounds weight was obtained. This was shipped to the University, where it was powdered and sampled for analysis. The samples since their preparation have been preserved in glass-stoppered bottles, and it is believed that they have not materially lost in water content. Samples not selected by Prof. Knight were usually taken by the owner or someone connected with the management and are indicated by the letter O; for them, of course, the University assumes no responsibility, although there is no reason to doubt the fairness of the selection. If any important coal-mines have been omitted from this investigation it is not the fault of the University, as announcements of the work in progress and requests for samples have been often published during the past two years.

\*The best brief account of thermo-chemical principles and processes known to the writers is Bertholet's "*Traite Pratique de Calorimetrie Chimique*."

†The coal samples obtained in 1894 were burned in the freight car in Laramie.

## EXPLANATION OF TERMS.

There are so many different units of heat and energy in use that it was thought necessary to calculate results in three of the more common forms to facilitate comparison.

A *calorie* is the amount of heat required to raise the temperature of one gram of water one deg. centigrade. The conception can, however, be generalized, and the statement that a gram of coal produces 6,000 cal. may be interpreted to mean that the heat produced by the combustion of one pound of coal would raise the temperature of 6,000 pounds of water 1 degree C. (1.8 Fahrenheit) or 600 pounds of water 10 degrees, etc.

A *foot-pound* is the amount of work required to raise the weight of one pound to the height of one foot against the force of gravity. A horse-power is 33,000 foot-pounds per minute, so dividing the number of foot-pounds per pound by 33,000 will give the number of horse-power developed by burning a pound of coal per minute. Of course only a very small fraction of the potential energy of the fuel can be converted into mechanical energy by even the most perfect heat engines known.

The third column gives the number of pounds of water which could be evaporated or converted into steam by the combustion of one pound of the coal under a pressure of one atmosphere; the water being regarded as already heated to the boiling-point, 100 C. or 212 Fahr.

## THE COAL TESTS.

The accompanying table gives all the coals so far tested, arranged in the order of their heating value. The figures given represent the total amount of heat obtainable by perfect combustion. No more heat can be obtained from the

fuel by any method of firing; on the contrary, as shown below, only about half the heat can be made available in steam production, and in common practice a still smaller proportion is usually obtained. In general, a larger proportion of the total amount of heat can be obtained from a good coal than from a poor one. In some cases, however, as where slow burning is required, a coal containing a considerable quantity of ash or even water will give better results than one of greater heating power per ton.

It should be borne in mind that the table gives the amount of heat, not the intensity, as that depends on the rate of combustion. The highest degree of heat attained in these tests was apparently from the pine knot which burned so fiercely as to melt into a ball the end of a platinum rod of 1.8 mm. diameter. In one respect there is an important difference between the conditions of combustion in the calorimeter and in the open furnace. In the calorimetric bomb the water contained in the coal and the gaseous products of combustion are cooled down to the ordinary temperature while in a furnace the steam and heated gases pass off. To represent their true relative value, therefore, the numbers given should be reduced in proportion to the amount of water contained. In the case of a coal giving 6000 calories but containing 10 per cent. water and four per cent. hydrogen, the correction would be 283 calories or about 4.7 per cent.



TABLE OF THE HEATING POWER OF WYOMING COALS.

Rank.	OWNER.	LOCATION.	NAME OF MINE.	Collector.	Calories per gram.	Pound-pounds per Pound of coal.	Pounds of water at 212°F evaporated by 1 lb coal.
1	J. D. Curtis	Ham's Fork, Uinta Co.	(Prospect sample)	O	7560	10,566,000	14.70
2	Wm. Goodell	" " "	(Six-foot face sample)	O	7467	10,435,000	13.90
3	A. Kendall	" " "	(Prospect sample)	O	7372	10,303,000	13.72
4	Sweetwater Coal Co.	Hopkins, Sweetwater Co.	Sweetwater	K	7358	10,284,000	13.69
5	F. Kindt	Rankin, Carbon Co.	Kindt No. 1	K	7140	9,978,000	13.29
6	Van Dyke Coal Co.	Rock Springs, Sweetwater Co.	Van Dyke (lower vein) (1893)	K	7132	9,967,000	13.27
7	" " "	" " "	" " No. 1 (:894)	O	7110	9,937,000	13.24
8	F. Kindt	Rankin, Carbon Co.	Kindt No. 2	K	7108	9,934,000	13.23
9	Van Dyke Coal Co.	Rock Springs, Sweetwater Co.	Van Dyke No. 2 (1894)	O	6963	9,730,000	12.96
10	McCoid	Rankin, Carbon Co.	McCoid	K	6952	9,716,000	12.94
11	Van Dyke Coal Co.	Rock Springs, Sweetwater Co.	Van Dyke (upper vein)(1893)	K	6922	9,675,000	12.89
12	Buffalo Fork Coal Co.	Fremont Co.	(Surface coal)	O	6896	9,638,000	12.84
13	Dillon Coal Co.	Rawlins, Carbon Co.	New Dillon Mine	O	6839	9,558,000	12.73
14	Rock Springs Coal Co.	Rock Springs, Sweetwater Co.	No. 2	K	6822	9,534,000	12.70
15	Union Pacific Coal Co.	" " "	Rock Springs No. 1	K	6812	9,521,000	12.68
16	" " "	" " "	" " 4	K	6728	9,403,000	12.52
17	" " "	" " "	" " 8	K	6705	9,371,000	12.48
18	" " "	" " "	" " 7	K	6704	9,370,000	12.47
19	Dillon Coal Co.	Rawlins, Carbon Co.	Dillon No. 2	K	6616	9,246,000	12.31
20	Cambria Coal Co.	Cambria, Weston Co.	Antelope	K	6566	9,177,000	12.22
21	" " "	" " "	Jumbo	K	6557	9,164,000	12.21

TABLE OF THE HEATING POWER OF WYOMING COALS—Continued.

Rank.	OWNER.	LOCATION.	NAME OF MINE.	Collector.	Calories per gram.	Foot-pounds per pound of coal.	Pounds of water at 212°F evaporated by 1 lb coal.
22	Rocky Mountain Coal & Iron Co.	Red Canon, Uinta Co.	Red Canon No. 6	K	6553	9,138,000	12.20
23	Union Pacific Coal Co.	Carbon, Carbon Co.	Carbon No. 2	K	6500	9,084,000	12.10
24	"	Rock Springs, Sweetwater Co.	Rock Springs No. 3 (E. face)	K	6436	8,995,000	11.98
25	"	Hanna, Carbon Co.	Hanna No. 1 (market sample)		6427	8,981,000	11.96
26	W. M. Carter	Casper, Natrona Co.	Casper No. 1	O	6400	8,945,000	11.91
27	Rocky Mountain Coal & Iron Co.	Red Canon, Uinta Co.	Red Canon No. 5 (lower 9 ft.)	K	6340	8,861,000	11.80
28	Terry Fee	Dutton Creek, Albany Co.	Brown (1893)	O	6164	8,615,000	11.47
29	G. L. Young	Rock Springs, Sweetwater Co.	(Sample No. 1)	O	6160	8,609,000	11.46
30	Union Pacific Coal Co.	Almy, Uinta Co.	Almy No. 7 (sample No. 2)	K	6145	8,588,000	11.44
31	G. L. Young	Rock Springs, Sweetwater Co.	(Sample No. 2)	O	6116	8,547,000	11.38
32	Dillon Coal Co.	Rawlins, Carbon Co.	Dillon	K	6046	8,450,000	11.25
33	L. R. Meyer	Carbon, Carbon Co.		O	6039	8,440,000	11.24
34	Union Pacific Coal Co.	Almy, Uinta Co.	Almy No. 7 (lower vein)	K	6017	8,410,000	11.20
35	L. A. Mason	Felix, Wyoming		O	5962	8,332,000	11.10
36	G. L. Young	Rock Springs, Sweetwater Co.	(Sample No. 3)	O	5949	8,314,000	11.07
37	Lander Fuel Co.	Popo Agie River, Fremont Co.		K	5938	8,299,000	11.05
38	Rocky Mountain Coal & Iron Co.	Red Canon, Uinta Co.	{ Red Canon No. 5, middle 2 1/2 feet. }				
39	Black Buttes Coal Co.	Black Buttes, Sweetwater Co.	Black Buttes No. 1	K	5933	8,292,000	11.04
40	J. D. Woodruff	Popo Agie River, Fremont Co.	Gilmore	O	5926	8,282,000	11.03
41	Terry Fee	Dutton Creek, Albany Co.	Brown (1894)	K	5886	8,226,000	10.96
42	Sheridan Fuel Co.	Sheridan, Sheridan Co.	Burgess	O	5734	8,014,000	10.67
				K	5723	7,998,000	10.65

TABLE OF THE HEATING POWER OF WYOMING COALS—Continued.

Rank.	OWNER.	LOCATION.	NAME OF MINE.	Collector.	Calories per gram.	Pound-pounds per foot of coal.	Pounds of water at 212°F. evaporated by 1 lb. coal.
43	J. D. Harper	Sundance, Crook Co.	Harper	O	5700	7,966,000	10.61
44	" "	" "	"	K	5680	7,938,000	10.57
45	Earl and Gillis	Pepo Agie River, Fremont Co.	Gillis	K	5631	7,810,000	10.48
46	Sheridan Fuel Co.	Sheridan, Sheridan Co.	Grinnell	K	5416	7,569,000	10.08
47	Deer Creek Coal Co.	Glenrock, Converse Co.	Deer Creek	K	5410	7,560,000	10.07
48	Inez Coal Co.	Inez, Converse Co.	Inez	K	5402	7,550,000	10.05
49	Chase and Farrell	Mill Creek, Albany Co.	Chase	O	5402	7,550,000	10.05
50	Mr. Bohack	Lost Soldier, Carbon Co.	Bohack	O	5375	7,512,000	10.00
51	J. F. Becker	Goose Creek, Sheridan Co.	Becker	K	5345	7,470,000	9.95
53	W. H. Holland	Buffalo, Johnson Co.	Holland	K	5293	7,397,000	9.85
53	Monker & Mathers	" "	Buffalo	K	4966	6,940,000	9.25
54	Diamond Coal Co.	" "	Diamond	K	4931	6,891,000	9.18
			<i>Average of Wyoming Coals</i>		6282	8,779,000	11.70

## TESTS OF OTHER FUELS.

Max Elser	Bowie, Texas
" "	" "
Elser (coal)	8,727,000
Webb (coal)	8,689,000
(Fat pine knot)	8,436,000
	11.62
	11.57
	11.23

# TABLE OF PROXIMATE ANALYSES

—OF—

## WYOMING COAL.

Rank in Heat- ing Power.	NAME OF MINE.	Water.	Volatile Com- bustible Matter.	Fixed Carbon.	Ash.	Sulphur.	Total Fuel.
1	J. Curtis, Ham's Fork	1.50	37.90	57.75	2.85	1.00	95.65
2	Wm. Goodell, Ham's Fork	2.95	38.00	54.00	4.05		92.00
3	A. Kendall, " "	3.75	37.25	55.40	3.60	.60	92.65
4	Sweetwater Mine	5.55	36.95	55.70	1.80	.86	92.65
5	Kindt No. 1	4.87	35.68	55.15	4.30	.77	90.83
6	Van Dyke (lower vein)	6.25	34.50	56.50	2.75	.74	91.00
8	Kindt No. 2	5.40	35.80	55.65	3.15	.70	91.45
10	McCoid	5.05	34.75	56.15	4.05	.85	90.90
11	Van Dyke (upper vein)	5.67	35.73	56.85	1.75	.68	92.58
13	New Dillon	7.25	33.25	54.25	4.25	.50	87.50
14	Rock Springs No. 2	6.22	34.78	55.75	3.25	1.41	90.58
15	" " " 1	5.38	36.42	55.60	2.60	.63	92.02
16	" " " 4	5.95	34.55	56.10	3.40	1.00	90.65
17	" " " 8	5.95	35.70	55.75	2.55	.65	91.45
18	" " " 7	6.37	35.18	54.85	3.60	.86	90.03
20	Antelope, Cambria	6.72	39.38	44.25	9.05	3.79	83.63
21	Jumbo, "	5.72	40.13	43.65	10.50	4.57	83.78
22	Red Canon No. 6	7.75	35.10	50.60	6.55	.29	85.70
23	Carbon No. 2	7.42	35.43	48.30	8.85		83.73
24	Rock Springs No. 3 (east face)	7.17	33.58	55.60	3.65	.83	89.18
26	Casper No. 1	11.30	32.10	53.55	3.20	.40	85.65
27	Red Canon No. 5 (lower 9 feet)	7.42	36.08	48.50	8.00	.44	84.58
28	Brown	11.85	34.65	47.30	6.20	1.25	81.95
29	G. L. Young No. 1	14.66	31.51	50.85	1.98	.56	82.36
30	Almy No. 7 (upper vein)	7.37	34.88	48.75	9.00		83.66
31	G. L. Young No. 2	14.64	36.70	46.45	2.21	.48	83.13
33	Meyer, Carbon	11.15	33.10	53.00	2.75	.65	83.10



PROXIMATE ANALYSES OF WYOMING COALS—*Continued.*

Rank in Heat- ing Power.	NAME OF MINE.	Water.	Volatile Com- bustible Matter.	Fixed Carbon.	Ash.	Sulphur.	Total Fuel.
34	Almy No. 7 (lower vein)	8.82	33.55	51.75	5.90	.65	85.30
35	Mason, Felix	10.50	37.02	48.46	4.42	.35	85.48
36	G. L. Young No. 3	14.23	37.48	46.07	2.22	.44	83.55
37	Lander Fuel Co.	11.40	36.60	47.60	4.40	.50	84.20
38	Red Canon No. 5 (middle 2½ feet)	6.81	36.49	47.45	9.25		83.94
39	Black Buttes No. 1	14.45	30.07	51.98	3.50	.61	82.05
40	Gilmore Mine	13.12	33.13	50.40	3.35		83.53
41	Brown (1894)	11.25	36.85	45.00	6.90	1.13	81.85
42	Burgess, Sheridan	13.05	37.55	44.70	4.70	.71	82.25
44	Harper, Sundance	7.88	33.52	43.90	14.70	1.03	77.40
45	Earl & Gillis	13.25	34.25	48.00	4.50	.71	82.25
46	Grinnell, Sheridan	14.42	33.18	44.75	7.65	2.87	77.93
47	Deer Creek, Glenrock	13.82	33.03	47.75	5.40	.61	80.78
48	Inez	14.65	26.05	42.50	6.80	.66	79.15
49	Chase	14.50	34.50	44.75	6.25	1.03	75.25
50	Bohack	13.65	39.25	42.60	4.50	.80	81.85
51	Becker, Sheridan	14.10	35.25	38.75	11.90	1.04	74.00
52	Holland, Buffalo	13.55	35.05	45.30	6.10		80.35
53	Monker & Mathers, Buffalo	14.70	34.30	44.20	6.80	.34	78.50
54	Diamond, Buffalo	14.50	33.35	44.30	7.85	.42	77.65

NOTE—To show in how far the heating power of coal is indicated by the ordinary proximate analysis we give here analyses of the same samples in the same order. These analyses are by Prof. Knight and have many of them been published in Bulletin No. 14 of Wyo. Agricultural Experiment Station. Nos. 27, 31, 36 and 39 and all sulphur determinations are by E. E. Slosson.

## EFFICIENCY OF BOILERS.

In practice we find that coal does not give its theoretical evaporation value. This is caused by many things that enter into the trial. Some of these can be modified so as to produce higher results than commonly given.

Many coals split up into fine particles when thrown directly upon the incandescent fuel upon the grate, and will pass through unconsumed. In ordinary methods of firing the kindling is at the bottom and the upper layers are at first only heated enough to drive off the volatile parts; these pass out of the furnace unconsumed unless special provision is made to introduce fresh air to mingle with the gases and burn them as fuel.

An insufficient supply of air to the incandescent fuel will also cause a loss that is very great and is usually wholly unnoticed; if the fuel is burned to carbonous oxide,  $\text{CO}$ , instead of carbonic acid,  $\text{CO}_2$ , the heat generated will be only 29,000 calories instead of 96,960 calories.

Radiation and conduction of heat from the boiler setting has been considered as a source of much loss; as high as 24 per cent. in some cases has been found.

After all precautions as to supply of air, grate setting and loss from radiation have been taken, the other losses are due largely to the fireman. One who understands what is taking place in the furnace and applies his knowledge will soon save in use of fuel the increase of wages over that of a poor fireman.

To show the difference between the theoretical and practical results obtained the following data are given:

In two tests made with compound locomotives by Geo. H. Barus, in April, May and June, 1890: Coal giving a calorimeter test of 7,634 calories, by a well-planned sta-

tionary boiler evaporated 11.7 pounds of water (at and from 212 degrees F.) In one locomotive 7.69 pounds of water evaporated and in the other 6.7 pounds of water evaporated. This gives for stationary boiler 82 per cent. of efficiency, for one locomotive 54 per cent. and the other 47 per cent.

Coals may be divided into five general classes; these classes as collated by Scheurer-Kestner and others are as follows:—†

	Actual calories.	Boiler test calories.	Per cent. Realized.
Dry or semi-bituminous Anthracite.....	9,200 to 9,600	5,760 to 6,080	63.9 per cent.
Short-flaming caking or coking.....	9,300 to 9,600	5,888 to 6,400	65 per cent.
True caking or coking.....	8,800 to 9,300	5,376 to 5,888	62.2 per cent.
Long-flaming or gas coal.....	8,500 to 8,800	4,864 to 5,312	58 per cent.
Long-flaming dry coals.....	8,000 to 8,500	4,288 to 4,800	55 per cent.

\*An average of 8 tests with boilers of standard make gave 10.45 pounds of water evaporated per pound of coal.

An average of 104 vertical boilers gave 12.24 pounds of water evaporated per pound of coal.

An average of 73 horizontal boilers gave 11.27 pounds of water evaporated per pound of coal.

These tests show what we may expect from an average of good coals under best conditions of boilers and careful management.

\*Taken from Weisbach's Mechanical Engineering.

†Kent in Mineral Industry for 1892. The coal is calculated as free from ash and water.

The comparisons would be of more value if the heating power of the coals had been given.

In these boiler tests it is shown that only 45 per cent. to 85 per cent. of theoretical evaporation power is obtained in practice.

In a recent test made with a Heine boiler with two kinds of coal two results are shown: with coal of 6,111 calories it gave 66 per cent. efficiency and with coal of 7,344 calories it gave 76 per cent. efficiency.

If these results be carefully studied it shows this fact plainly: the better the quality of the fuel the greater the efficiency of the boiler, thus giving double results from the use of the heat fuel; not only is there a gain in amount of fuel saved but also a gain in efficiency.

In the use of Wyoming coal for power purposes somewhat different management is needed than with the eastern coal. As they have but little coking properties upon the grate they have a tendency to split up into small pieces and pass through the bars; this is easily overcome by using fine grate bars. The splitting up has also a tendency to cause smothering of the fire; this may be prevented by having a wide dead plate in front on to which most of the fuel is placed; here it is gradually heated and the volatile parts in passing off have to pass over the ignited coal upon the grate and will be entirely consumed, if proper arrangement is made to supply fresh air. The heated coal can then be pushed back upon the bars.

Thin fire-bed with frequent firing also gives best results; regulation of draft is best accomplished with the use of a damper in the stack rather than by ashpit and furnace doors.

With our vast coal-fields but little prospected and the



large yield of coal from those already opened it would seem as if efforts to obtain highest efficiency are not necessary, but when we consider that the cost of fuel per ton is greater than in eastern States, our manufacturers must bring down the cost of operation in every way possible if they wish to hold the western market against eastern manufacturers, and this can be done by using the most efficient motive power and the best fuel they can obtain, when the amount of actual fuel is estimated per ton of coal purchased.

With two methods of obtaining draught we obtain two different results from burning the same kind of coal with the same boiler. In practice it is found that more air must be supplied than is theoretically required. With natural draught about 24 pounds of air should be supplied per pound of fuel used, while 18 pounds is found sufficient when a blower is used.

#### PETROLEUM AS FUEL.

The use of liquid fuel is rapidly increasing during the last three years, the most notable example in this country being that of the power plant of the World's Fair at Chicago; not being able to obtain the official report we can give no actual data as the results. In Russia many of the railroads and the steamers on the Black Sea are now being fired with petroleum or the heavy refuse oils from the refineries.

From the table below it can be seen that pound for pound the oils of Wyoming possess nearly double the heating capacity of the coals. In the use of oil for steaming purposes the chief advantages are: ease with which firing can be controlled—simply turning a valve will adjust the heat to the desired degree; economy of storage room; freedom from dirt and refuse from firing.

No complex apparatus is necessary to use oil as fuel. Any method of reducing the oil to a fine spray with either air or steam and of adjusting amount of air necessary for combustion are all that are required. This may be made by any steam-fitter from ordinary steam-pipe and fittings. No change, or but little, is needed with boilers as ordinarily set to use the oil as it may be introduced into the furnace through pipes that may pass through the boiler front or through the sides of the fire-box.

The use of oil on the railroads of Russia has proved economical because fewer delays are caused in loading up with fuel and no fuel is needed while trains are stopping at stations; the steam pressure can be more easily controlled and no steam is wasted at the safety valve. As the Wyoming oils are much like the Russian oils the same results may be expected with their use.

The use of oil in iron manufacture is increasing rapidly. In the Ohio iron manufactories oil is considered cheaper at 2 cts. per gallon than coal at \$2.00 per ton for heating furnaces in making bolts, spikes, chain and other small work.

A comparative commercial test of coal and oil for heating is much to be desired in connection with calorimeter tests. This would show exactly the relative value of the two under ordinary conditions.

# WYCMING PETROLEUM AND ASPHALT.

Rank.		LOCATION.	MINE.	Calories per Gram.	Foot-pounds per pound of oil.	Pounds of water at 212°F evaporated by 1 lb oil.
1	Petroleum		Bonanza	10.927		
*2	"	Shoshone Reservation		10.883	15,204,000	22.24
*3	"	Salt Creek, Natrona Co.		10.813	15,106,000	20.11
*4	"	Oil Mountain, Natrona Co.		10.743		
*5	"	Newcastle, Weston Co.		10.447	14,595,000	19.43
*6	"	Little Popo Agie, Fremont Co. }	Murphy Wells	10.430	14,571,000	19.40
7	Asphalt			9.532		
*8	"	Wallace Creek, west of Garfield Park		6.307		

\*Collected by Prof. Knight.

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METHODS OF DETERMINING HEATING POWER.

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There are in use three methods of estimating the heating value of fuels: boiler tests, calculation from analysis and calorimeter tests.

1. The boiler test. By using a weighed amount of the coal in question under as nearly as possible the same conditions as other coals we get a satisfactory practical knowledge of its fitness for the purpose. The disadvantages of this method are the difficulty and expense of testing a large number of samples in this way, and the fact that since only a small proportion of the heat can be obtained in its equivalent of steam pressure or mechanical movement, the experiment is always a test of the efficiency of the furnace and boiler and of skill in firing, instead of a determination of the absolute value of the fuel. In other furnaces or under other conditions the results might be reversed. It is only in an experimental plant where all the factors, such as the temperature and volume of the entering air and escaping gases, composition of the coal, temperature of the water and pressure of the steam, losses from radiation, etc., can all be measured, that the absolute heating power can be found. With accurate work under such conditions the total amount can be accounted for to within a few per cent.\*

2. Calculation of heating power from chemical analyses. The proximate analysis of coal gives, as may be seen from the tables of analyses and calorimetric tests in this bulletin, a fair idea of the relative value, since of course the greater the amount of water and ash the less the per cent. of fuel. No accurate valuation can, however, be made on the basis of proximate analysis, since the composition of the volatile combustible matter and even of the "fixed carbon"

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\*Rowan and Mills: Fuels. Page 731.



is not definite and the dividing line is not exact. Elementary analysis affords a better basis for the calculation, and if the sample belongs to a well-defined class which has been sufficiently studied, the application of the proper formula usually gives a close approximation to the calorimetric result.\* No formula can of course give exact results because the elements, carbon, hydrogen and oxygen, exist in compounds having different heats of formation and consequently of combustion. Elementary organic analysis is a much longer and more delicate process than the direct determination of heating value with the calorimeter.

3. Calorimetric tests. The most satisfactory method of finding the heating power of a fuel is to burn a small sample under such conditions as admit of measuring the amount of heat evolved. This is done by carrying on the combustion inside a vessel filled with a known weight of water of a certain temperature. There are two kinds of combustion calorimeters; in one the fuel is mixed in a small diving-bell with salts such as potassium chlorate and nitrate which supply the oxygen, in the other it is burned in compressed oxygen.

An instrument of the first class, Thompson's calorimeter, has on account of its cheapness and convenience been extensively employed in England and the United States in the valuation of fuels. The process is liable to many errors, some of which, being variable, it is impossible to correct. These errors are chiefly due to losses of heat through the escaping of imperfectly cooled gases, the solution of the oxygen salts and their products in the water, irregular heat-

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\*The difference is about 3 per cent. See a valuable article by Wm. Kent on the heating power of coal in *The Mineral Industry* for 1892, Vol. I, page 97.

ing of the thick glass vessel, and particles of carbon which are kept from burning by the melting salts. The correction for loss of heat is stated by the manufacturers to be 10 per cent.; it has been estimated,\* however, at 30 per cent. and in fact no constant correction can be used. In using the instrument on Wyoming coals we found it necessary to add a considerable quantity of some auxiliary combustible which complicates the reactions. Even when it is constructed for scientific instead of technical work and the most elaborate precautions are taken as in Stohmann's investigations† a calorimeter of this kind gives inferior results and it is now abandoned in favor of the simpler and more exact bomb calorimeters.

#### DESCRIPTION OF THE BOMB CALORIMETER.

The essential conditions for the determination of heat of combustion are that the product be completely burned, that the heat pass entirely into the water of the calorimeter vessel and that the combustion be as quick as possible. These conditions are best attained by the process devised by Berthelot, according to which the combustion takes place in a closed steel vessel (the so-called bomb) filled with oxygen under twenty to twenty-five atmospheres pressure and almost entirely immersed in the water of the calorimeter. Under these circumstances a hydrocarbon burns completely to carbon dioxid and water in a few seconds, none of the products of combustion can escape and the heat passes into the surrounding water in the course of two or three minutes. The high price of Berthelot's calorimeter, about \$1,500, has prevented it from coming into common use. In June, 1892,

\*L. I. Blake: Kansas Academy of Sciences, 1888, page 42.

†Kalorimetrische Untersuchungen von F. Stohmann, Landwirthschaftliche Jahrbucher, 13, page 513.

an account was published\* of a modification of Berthelot's apparatus invented by M. Mahler in which the expensive platinum lining of the bomb was replaced by a thin coating of enamel without impairing the efficiency of the instrument. § A calorimeter of this kind was procured by the University of Wyoming† in July, 1894, for the study of the coal and petroleum of the State and for use in food investigations in the Agricultural Experiment Station.

As we have had many inquiries about this instrument and its workings we give a description with a cut.

The bomb (B in cut) of our apparatus is 15 centimeters high and ten cm in diameter, with an average thickness of eight mm. It is Martin-Siemens soft-forged steel of a resistance of 50 kilogrammes per square millimeter of square section and 20 per cent. elongation. It is nickel-plated on the outside and coated on the inside with a thin white enamel to prevent corrosion by the oxygen and the acids which are among the products of combustion. The capacity of the bomb is 580 cc. A platinum tray (C) of 30 mm in diameter and 5 mm in depth‡ is suspended from the cover by a rod of platinum. A similar rod passing through the cover but insulated from it reaches nearly to the tray and serves as the other electrode. The cover is screwed on over the top of the bomb and a hermetical joint secured by a ring of

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\*Bulletin de la Societe d'Encouragement pour l'Industrie Nationale, Paris.

†The apparatus is constructed by M. L. Golaz, Rue Saint-Jacques, Paris, and is sold at the following prices: Mahler's calorimeter complete 750 francs, pump for compressing oxygen 500 francs, pair of thermometers 50 francs. Our instrument was procured through Eimer and Amend, N. Y.

§A cheaper form of the bomb calorimeter which dispenses with pump or gas cylinder is described in Hempel's Gas Analysis.

‡This is heavier and deeper than the one sold with the apparatus.

lead. The oxygen is passed in through the stem of the needle valve, which is screwed down when the bomb is filled. The bomb is set in a support which touches the bottom of the calorimeter vessel on three points. The calorimeter vessel is a pail of thin brass, twenty-three centimeters high and fourteen centimeters in diameter. This rests on three points of a light wooden support and is surrounded by a large double-walled vessel covered with thick felt containing water at the normal temperature of the room. An ingenious stirring mechanism enables one to keep the water of the calorimeter in thermal equilibrium with slight effort. The calorimeter is so well isolated from external influences that the water often does not vary in temperature a hundredth of a degree in fifteen minutes, although the air of the room may be quite variable.

Two thermometers were used, one reading between eight and eighteen degrees C. and the other between eighteen and twenty-eight degrees; each degree covering a space of  $3\frac{1}{2}$  centimeters. They are graduated to a fiftieth of a degree and were read to one-hundredth, although with a glass they can be read to a much finer interval.

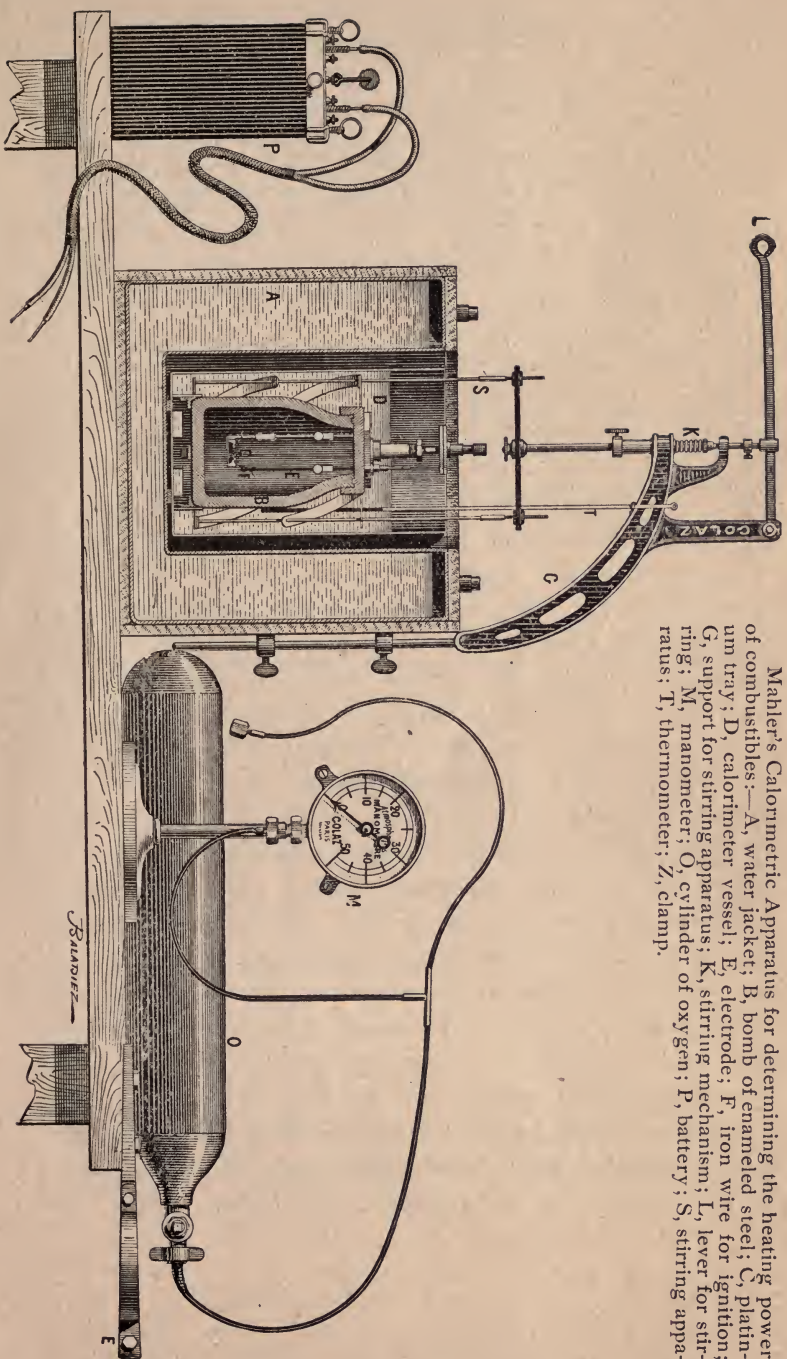
The oxygen used was made in the laboratory, purified by passing through a solution of caustic potash and three rolls of copper gauze, and kept in gas-bags; the slight correction indicated for Berthelot\* for the loss of heat through vaporization of water has not been applied.

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\*Comptes Rendus, 114, page 318.



Mahler's Calorimetric Apparatus for determining the heating power of combustibles:—A, water jacket; B, bomb of enameled steel; C, plain-um tray; D, calorimeter vessel; E, electrode; F, iron wire for ignition; G, support for stirring apparatus; K, stirring mechanism; L, lever for stirring; M, manometer; O, cylinder of oxygen; P, battery; S, stirring apparatus; T, thermometer; Z, clamp.



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THE PROCESS OF COMBUSTION.

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One gram of the coal or oil is weighed into the tared platinum tray which is then attached to the platinum rod in the calorimeter bomb. A piece of iron wire of known weight is stretched across from the rod supporting the tray to the insulated support and preferably touching the combustible or buried in it. The bomb is then placed in a lead-lined clamp and the top tightly screwed on by means of a wrench. The needle-valve is opened and connected with the compression pump by a long slender copper tube. Oxygen is then forced into the bomb until the manometer reads twenty or twenty-five atmospheres. The needle valve is closed and disconnected from the filling tube and the bomb is immersed in the water of the calorimeter. The water should be two to three degrees lower in temperature than the air of the room and the water in the jacket of the calorimeter, and a sufficient amount should be weighed out to cover the bomb nearly to the top of the insulated electrode. In our instrument 2,309 grams of water was usually taken, as that gave with the water value of the apparatus (491 grams) a convenient factor for calculation. The stirring apparatus is kept in motion and as soon as the change in temperature becomes constant readings of the thermometer are taken at intervals of one minute. At the end of the fifth minute the combustible is fired by passing an electric current through the iron wire raising it to redness. We used a plunge battery of six bichromate cells for this purpose. One wire is connected to the insulated electrode and the other is touched to some exposed part of the bomb. In about ten seconds the thermometer is observed to rise, rapidly at first, then more slowly, reaching a maximum usually on the second or third minute after firing. After the

maximum it falls regularly and slowly if the proper temperature has been chosen for the water, and readings are again made at intervals of a minute for five minutes more. Then the bomb is taken out of the calorimeter, the needle valve cautiously opened to allow the products of combustion and residual oxygen to escape; after which the bomb is opened and rinsed out with distilled water. The rinsings are titrated with a standard solution of potassium hydrate or sodium carbonate to determine the amount of nitric acid formed by the combustion, and if the combustible contains sulphur the solution is set aside for determination of sulphuric acid. The whole operation including the weighing of the sample and pumping in the oxygen can be completed in less than an hour if everything works well.

Multiplying the weight of water taken plus the water value of the apparatus by the corrected rise in temperature gives the heat of combustion of one gram of the substance, subject to the corrections mentioned below.

#### CORRECTIONS.

1. *Correction for the influence of the temperature of the environment.* This is the largest and most important correction to be made, although on account of the short interval during which the temperature rises, usually two minutes, it is smaller in this process than in any other.

As there is no way of measuring directly the amount of heat lost or gained by the calorimeter from the moment of firing to the moment when all the heat of combustion has been given up to the water surrounding the bomb, it is necessary to calculate this from the rate of change of temperature before firing and the rate of change when the temperature has come again to equilibrium. This correction is most



accurately given by the application of the Regnault-Pfaundler formula. If the preliminary period and the final period are each five minutes, with readings of the thermometer every minute, the correction according to this formula is:\*

$$\left[ t_5 - t_7 + \dots + t_{N-1} - \frac{t_5 + t_N}{2} - (N-5)t_m \right] \frac{D-d}{T-t_m} + (N-5)d$$

where  $t$  indicates the temperature at the end of the minute designated by the subscript;  $t_5$  is the instant of firing;  $N$  is the number of the maximum reading;  $t_m$  is the average of the five readings before firing;  $T$  is the average of the readings of the final period;  $D$  is the average change in temperature during the final period, and  $d$  is the average change in temperature during the preliminary period.

As in practice the maximum temperature nearly always occurs on the seventh, the eighth or the ninth moment, the formula can be reduced for these three cases to the following forms, which are easy to calculate:

When the maximum is the end of the seventh moment the correction for the loss or gain of heat during the minutes 5-6 and 6-7 is

$$\frac{1}{5} \left\{ \frac{[(2t_5 + t_7) - (2t_6 + t_8)] [(t_7 + t_8) - (t_6 + t_{12})]}{(t_{12} + t_7) - (t_6 + t_{12})} - 2(t_6 - t_5) \right\}$$

When the maximum is the eighth moment the loss or gain for the minutes 5-6, 6-7, 7-8 is

$$\frac{1}{5} \left\{ \frac{[(2t_5 + 2t_7 + t_8) - (3t_6 + t_9)] [(t_8 + t_9) - (t_{13} + t_6)]}{(t_{13} + t_8) - (t_6 + t_9)} - 3(t_6 - t_5) \right\}$$

When the maximum is the ninth minute the loss or gain for the minutes 5-6, 6-7, 7-8, 8-9, is

$$\frac{1}{5} \left\{ \frac{[(2t_5 + 2t_7 + 2t_8 + t_9) - (4t_6 + t_{10})] [(t_9 + t_{10}) - (t_{14} + t_6)]}{(t_{14} + t_9) - (t_6 + t_{10})} - 4(t_6 - t_5) \right\}$$

This correction becomes a minimum when the temperature before firing is rising about three times as fast as it falls after the maximum.

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\*Ostwald: Lehrbuch der Allgemeinen Chemie, 2nd Ed., Vol. I, page 572



As the period of combustion is so short M. Mahler has given a method of correction based on Newton's law which gives results sufficiently exact for technical work. His rules are:\*

1. The law of decrease of temperature observed after the maximum represents the loss of heat before the maximum and for any given minute on condition that the mean temperature of this minute does not differ more than one degree from the maximum temperature.

2. If the temperature of the given minute differs by more than one degree but less than two degrees from that of the maximum, the number that represents the law of decrease at the moment of the maximum less 0.005 will give the desired correction.

A comparison of the two methods in some twenty cases showed an average difference of 0.0013, which on one gram naphthalene would amount to about three calories, or .03 of one per cent.; a difference within the limit of error in technical work. In this bulletin the Regnault-Pfaundler formula has been used for determining the constants of the apparatus and Mahler's for most of the coals and oils.

2. *Correction for formation of nitric acid.* About fifty milligrams of nitric acid are formed from the nitrogen of the air by the combustion, and it is necessary to ascertain the amount of this and subtract the heat of formation, 227 cal. per gram, from the heat of combustion of the substance under examination. This is estimated by titration with a standard alkali solution containing 3.706 grams of sodium carbonate,  $\text{Na}_2\text{CO}_3$ . One cubic centimeter of this solution is equal to .0044 grams nitric acid of which the heat of

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\*Bulletin de la Societe d'Encouragement pour l'Industrie Nationale, June, 1892, page 335.

formation is one calorie, so the number of cubic centimeters required to titrate the washings of the bomb can be written at once as calories. Methyl orange is used as an indicator.

3. *Correction for the combustion of the iron wire.* The combustion of the small piece of iron wire used to ignite the combustible adds to the apparent rise in temperature, and correction must be made by taking a known weight of wire and subtracting its heat of combustion. A No. 32 to 36, Brown and Sharpe gauge, is suitable, and it is preferable to use the copper-plated wire, as the plain wire easily becomes oxydized on the surface. Of No. 36 wire one meter weighs .3160 grams; of this in our experiments we used a length of 4.8 centimeters, giving a heat of combustion of 25 calories.

The heat of combustion of iron under these circumstances is stated to be 1650 cal. per gram.\* This is on the assumption that all the iron is burned to  $\text{Fe}_3\text{O}_4$ . That this is not correct is shown by the following analyses of the iron oxid resulting from some twenty combustions each: No. 1, 71.59 per cent. iron in oxid; No. 2, 75.81 per cent. iron in oxid. The first would correspond to 74.7 per cent.  $\text{Fe}_3\text{O}_4$  and 25.3 per cent.  $\text{Fe}_2\text{O}_3$ , while the second might be composed of 86.8 per cent.  $\text{Fe}_3\text{O}_4$  and 13.2 per cent. unburned iron. Other mixtures of iron and its oxids would of course give the same analytical results. The heat of combustion of ferric oxid is not exactly known, but it is certainly less than that of  $\text{Fe}_3\text{O}_4$ . It appears from this that the character of the oxids formed is variable and the ordinary correction consequently inaccurate by several calories. The error is not, however, as great as the analyses would seem to indicate, for it was only the larger particles such as could be easily picked off that were taken for analysis.

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\*Berthelot: *Traite Pratique de Calorimetrie Chimique*, page 139.

4. *Correction for sulphur.* The presence of sulphur in the combustible necessitates another correction, for the free sulphuric acid formed by the combustion of sulphur compounds will be titrated as nitric although its heat of combustion is different and the heat of the burning sulphur is a legitimate part of the heat of combustion of the fuel. The sulphuric acid must therefore be determined in the rinsings of the bomb after the titration for free acid and the heat of formation of its equivalent in nitric acid subtracted from the number obtained by titration. The weight of barium sulphate multiplied by 100 gives directly the number of calories to be subtracted.

Sulphur, however, exists in coal in three forms: organic sulphur compounds, pyrites, and sulphates, chiefly gypsum. Of these the third at least would not be converted into free acid by the combustion and the ordinary correction would be too great. The point is of especial importance in dealing with Wyoming coals, for although the percentage of sulphur is generally small yet it is more often in the form of gypsum than pyrites. Nevertheless, as to find the original state of the sulphur would require two analyses, the whole is regarded as forming sulphuric acid and the equivalent, usually amounting to about 5 cal., has been subtracted in all cases.

#### DETERMINATION OF WATER VALUE OF THE APPARATUS.

The heat produced by combustion is absorbed not only by the water in the calorimeter but also by the calorimeter vessel, the bomb, the stirring apparatus and thermometer in contact with it. But the amount of heat absorbed by them depends on their weight and material. It is therefore necessary to find the water value of the apparatus, that is,

what weight of water would absorb the same amount of heat for the same rise in temperature. This is done by multiplying the weight of the different parts of the apparatus by the specific heat of the material of which they are composed.\* In this case the calculation was as follows:

Calorimeter vessel	445 g.,	stirring apparatus	143 g.,	
588 g. brass	x .093	-	-	54.69
Bomb, 3,920 g. steel	x .1097	-	-	430.03
22.36 g. platinum	x .0324	-	-	.72
8 g. lead	x .031	-	-	.25
Thermometer, bulb 2.72 g., tube 33.56 g.,	1/4 im-			
mersed, 8.61 g. glass	x .184	-	-	1.58
35.36 g. mercury	x .033	-	-	1.17
Oxygen, (20 atmospheres pressure)	16.7 g. x .155†			2.59
Water value	-	-	-	491.03

Another method of determining the water value of a calorimeter is to burn in it certain compounds whose heat of combustion is accurately known. This has the advantage that the water value of the whole apparatus is determined directly and under the same conditions as in an ordinary combustion, but it has the disadvantage that the heat of combustion of no compound is exactly known. In determining the water value of our calorimeter we made twelve combustions with resublimed naphthalene, of which the heat of combustion as determined by Berthelot and his assistants is 9,692 calories. The average of the twelve combustions gave 491.4 grams as the water value of the calorimeter. One combustion with granulated sugar, using two g. and taking the heat of combustion as 3961.7 cal. per gram, gave 491 g. as the value. As all these are in satisfactory agreement the number 491 has been adopted as the water value. A difference of one

\*The weight of the enamel on the bomb was not known. The water value of the apparatus as calculated is therefore too low.

†Stohmann uses .2175, the specific heat for constant pressure, instead of .155, the specific heat for constant volume. *Journal für praktische Chemie*, 39, page 536.



gram in water value makes a difference of about .03 of one per cent. in the final result.

## AN EXAMPLE.

The method of calculating the heat of combustion may be made more clear by giving in detail an example in which the corrections are unusually large.

Coal No. 33. L. R. Meyer, Carbon. November 30, 1894.  
1 gram coal. .0250 g. wire. 2,300 g. water in calorimeter.  
Preliminary Period. Combustion Period. Final Period.

0—11.47	5—11.48	9—13.64
1—11.47	5½—12.50	10—13.63
3—11.48	6—13.34	11—13.62
4—11.48	7—13.63	12—13.62
5—11.48 Fired.	8—13.64	13—13.62
	9—13.64	14—13.61

Nitric acid=9.0 cc. sodium carbonate solution=9 cal.  
Weight BaSO<sub>4</sub>, .0472.

From the 9th to 14th reading .03 deg. heat was lost or .006 deg. per minute. Then for the three and a half minutes, 5½-6, 6-7, 7-8, 8-9, the total loss .0021 deg. The temperature rose .01 deg. during the preliminary period or .002 degree per minute. The correction for the half minute 5-5½ is therefore .001. The total rise in temperature is from 11.48 deg. to 13.64 deg. or 2.16 deg.; adding to this the correction .02 deg. gives 2.18 deg. for the true rise due to combustion. The water value of the apparatus, 491 g., added to the weight of water used, 2,300 g., gives 2,791 g., which multiplied by 2.18 gives 6,084.4 calories. The weight of the barium sulphate with the decimal point moved two places to the right gives 4.7 to be subtracted from 9.0 cal. leaving 4.3 cal. The weight of the wire, .0250 g., multiplied by 1650 gives 41.2 cal. The sum of the corrections for formation of iron oxid and nitric acid, 45.5, subtracted from 6,084.4 gives 6,039 calories for the

true heat of the combustion of one gram of the coal. The use of Regnault's formula in this case would make the rise of temperature 2.179 deg. and the heat of combustion 6,036.

#### NOTES ON CALORIMETRY.

The use of a cylinder of oxygen under great pressure such as is now in the market, dispenses with a compression pump, and shortens the time required for a combustion by one-half. It has the disadvantage that the quality of the oxygen is not as much under control as where it is made in the laboratory.

It is not necessary that the coal should be finely powdered, nor is there any difficulty in using fine samples. Of the samples used, one was in coarse fragments and some had been passed through a hundred mesh seine. In using very fine coal or freshly sublimed naphthalene, it is convenient to compress it into tablets with a "diamond mortar" such as is used in crushing minerals for analysis.

The cylinder of the compression pump must be kept cool by a water jacket, or the oil will become ignited by the compressed oxygen and an explosion result.

The rapidity with which the heat is given up to the water of the calorimeter is shown by the following average of ten determinations:

Heat given off during the period	5-5½	=	27.9	per cent.
" " " " " "	5½-6	=	50.3	" "
" " " " " "	6-7	=	20.1	" "
" " " " " "	7-8	=	1.7	" "
			100.0	" "

That is, 78.2 per cent. of the total heat is absorbed by the water during the first minute and 98.3 per cent. during the first two minutes.

Care must be taken to scrape off the iron oxid from the electrodes before attaching the new wire, as a very thin film will prevent ignition by the electric current.

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